Large scale ab initio molecular dynamics simulations of liquid and solid electrolytes

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June 12, 2019

Project ID
bat425

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Overview

Timeline

- Start: Oct.1 2016
- End: Sept. 31, 2019
- Percent complete: 85%

Barriers

- Poor understanding of the Li-S dissolution process
- Stable Li-S cathode material and design
- Stable solid electrolyte

Budget

- Funding for FY 17 $225K
- Funding for FY 18 $225K
- Funding for FY 19 $225K

Partners

- Prof. Yi Cui, Stanford
- Prof. Zhenan Bao, Stanford
- Dr. Gao Liu, LBNL
- Prof. Feng Pan, Beijing Univ.

Objective and Relevance

- Li-S battery has a large theoretical capacity (2546 Wh/Kg), but dissolution, low electric conductivity have prevented its commercialization
- Need a deeper understanding of the thermal dynamics of the dissolution
- Need novel designs of new Li-S cathode materials
- Theoretically design new Li-S cathodes, using thermodynamics to prevent dissolution
- Use other light elements and 2D materials to design novel cathodes
- Solid electrolyte can bring new designs for battery, but stability is one issue
- Use ab initio simulation to understand the Li diffusion in solid electrolyte, and to design more stable systems

Milestones

Month/Year	Milestones
12/2016	Set up Li_2S_n calculation with CPM solvent model (completed)
03/2017	Continue Li_2S_n calculation with direct AIMD simulation (completed)
06/2017	Study the dissociation of Li_2S_n, and Li_2S_n-solvent interaction (completed)
09/2017	Calculate the local minimum and transition path barrier height (completed)
12/2017	Calculate Li-S with carbon substrate (completed)
03/2018	Calculation of Li-S/carbon-nitride substrate (completed)
06/2018	Molecular dynamics simulation of Li-S in solvent and on substrate (completed)
09/2018	Design new cathode materials for Li-S (completed)
12/2018	Li diffusion in LiS/2D material sandwich structure (completed)
03/2019	Li diffusion in solid electrolyte and LiF layer (completed).

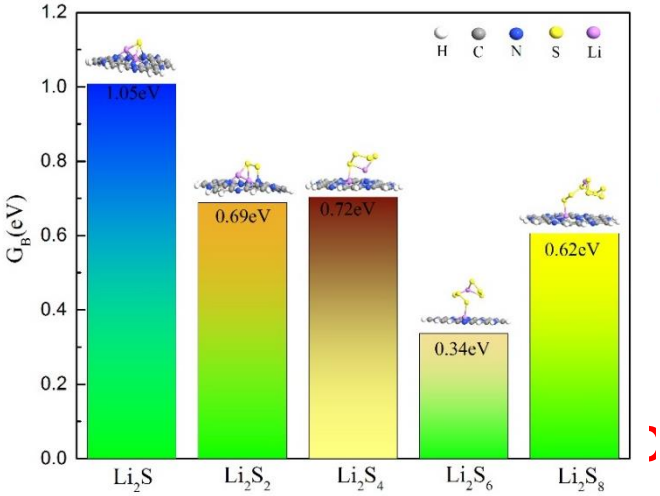
Approach

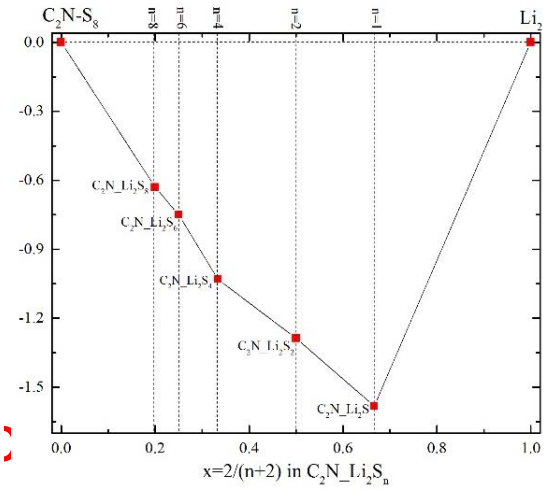
Using first principle simulation to understand the Li-S thermodynamics, to study Li diffusion, and to design new Li-S cathodes

- Use genetic algorithm to search for Li_2S_n cluster structure.
- Anchor Li_2S_n cluster on a substrate to prevent its dissolution based on thermodynamics phase diagram
- Use light elements and 2D materials to design novel Li cathodes
- Use ab initio molecular dynamics (AIMD) to study Li diffusion in cathode material and Li electrolyte
- Develop robust charge polarizable model (CPM) to describe the solvent effect
- Build model Hamiltonian to search for Li diffusion path and solid electrolyte in a high-throughput fashion
- Use thermodynamic integration to calculate the Gibbs free energies of different species
- Use genetic algorithm search to find surface structure for SEI
- Develop special algorithms to calculate Li diffusion barrier in amorphous cathode material

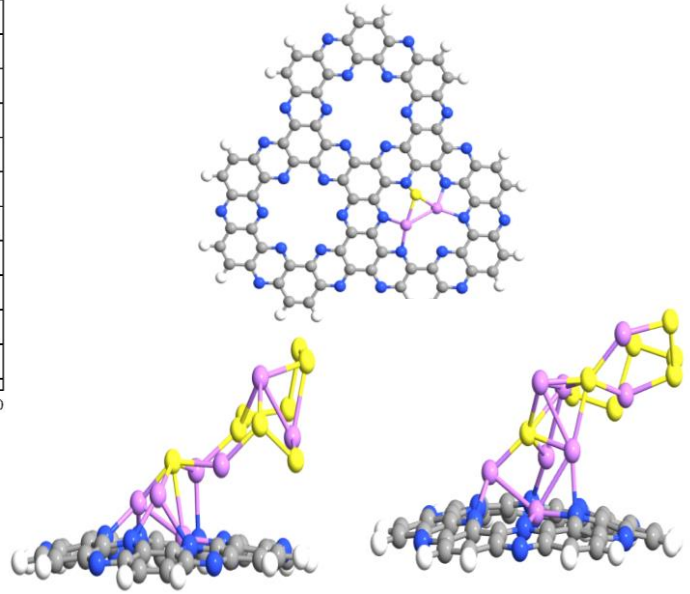
Accomplishments

Using C2N as Li-S cathode material





Using genetic algorithm to search the structure (fix the substrate).



The binding energy between the Li2Sn polysulfur and the C2N substrate (left), and the formation energy diagram (right) of $C_2N\_Li_2S_m$.

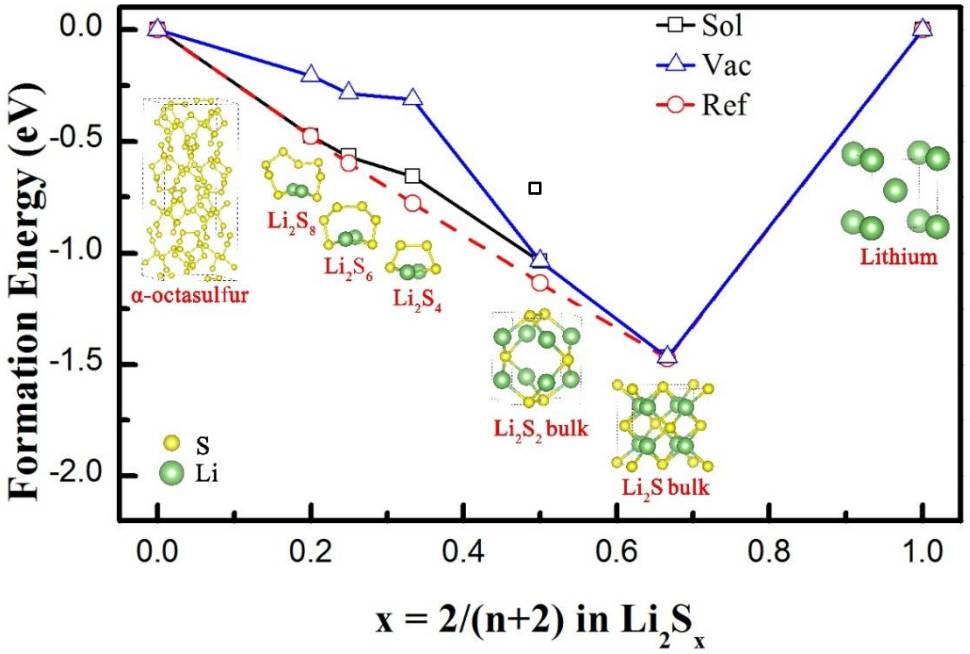
Thermodynamically stable against dissolution

Label	Category	Reactions (DEM/DOL (1 : 1 v/v))	ΔG (eV)	Feasibility
R_1	$C_2N\_Li_3S_8$	$C_2N\_Li_3S_8 \rightarrow Li\_C_2N + Li_2S_8$	1.73	No
R_2	$Li_5S_8\_C_2N$	$Li_5S_8\_C_2N \rightarrow Li\_C_2N + 2Li_2S_4$	2.23	No
R_3		$Li_5S_8\_C_2N \rightarrow Li_3\_C_2N + Li_2S_8$	6.64	No
R_4	$Li_7S_8\_C_2N$	$Li_7S_8\_C_2N \rightarrow Li_3\_C_2N + 2Li_2S_4$	10.06	No
R_5		$Li_7S_8\_C_2N \rightarrow Li_5\_C_2N + Li_2S_8$	7.36	No
R_6	$Li_{10}S_8\_C_2N$	$Li_{10}S_8\_C_2N \rightarrow Li_6S_6\_C_2N + 2Li_2S$	3.40	No
R_7		$Li_{10}S_8\_C_2N \rightarrow Li_8S_4\_C_2N + Li_2S_4$	3.20	No
R_8		$Li_{10}S_8\_C_2N \rightarrow Li_4\_C_2N + Li_2S_6 + 2Li_2S$	7.24	No
R_9		$Li_{10}S_8\_C_2N \rightarrow Li_4\_C_2N + Li_2S_4 + 2Li_2S_2$	3.95	No

J. Wu, L.W. Wang, J. Mater. Chem. A, 2018, 6, 2984

Accomplishments

Development of a better charge polarization solvent model based on experimental data



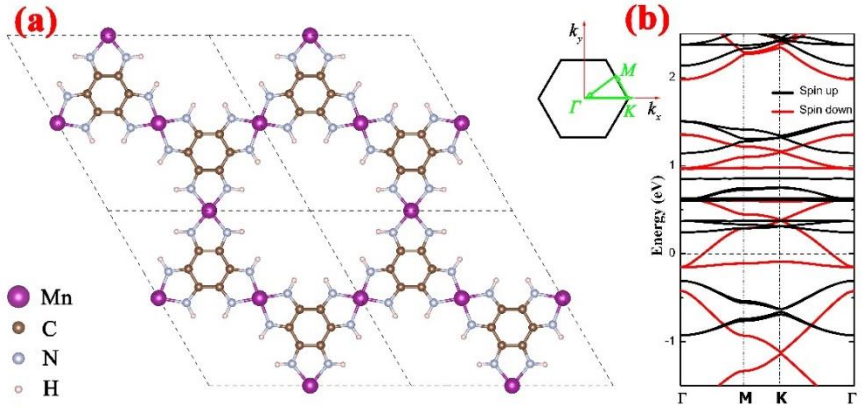
	exp	theory
$S_8 \rightarrow Li_2S_8$	2.39	2.39
Li_2S_8-Li_2S_6	2.37	1.92
Li_2S_6-Li_2S_4	2.24	1.36
Li_2S_4-Li_2S_2	2.20	2.18
Li_2S_2-Li_2S	2.15	2.33
S_8+Li-Li_2S	2.20	2.21

Experiment: vs calculated voltages (eV)

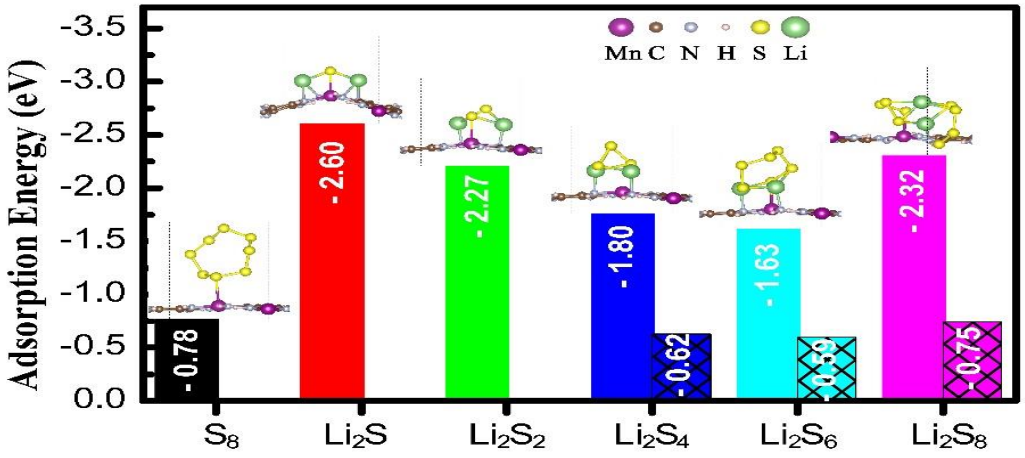
- **The experimental formation energy of bulk Li_2S is obtained by the α-octasulfur, and Li crystal structures**
- **Li_2S_2 should be crystal or larger cluster**
- **Li_2S_4, Li_2S_6, Li_2S_8 with solvent effect fit very well with experimental value**

Accomplishments

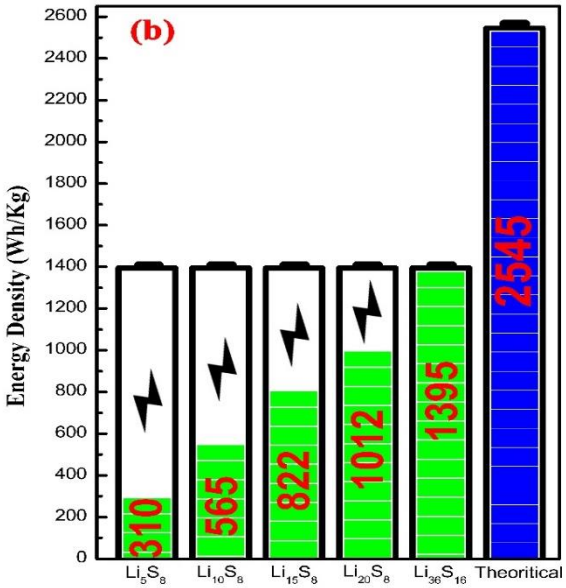
Using Mn-HAB-CP as 2D Li-S cathode



- **Conductive**
- **Transition metal:** Adsorption S.
- **Nitrogen:** Adsorption Li.
- **Porous:**



The adsorption energy of isolated S_8, and Li_2S_y on Mn-HAB-CP in the vacuum (bars without pattern) and solvent (bars with net pattern).

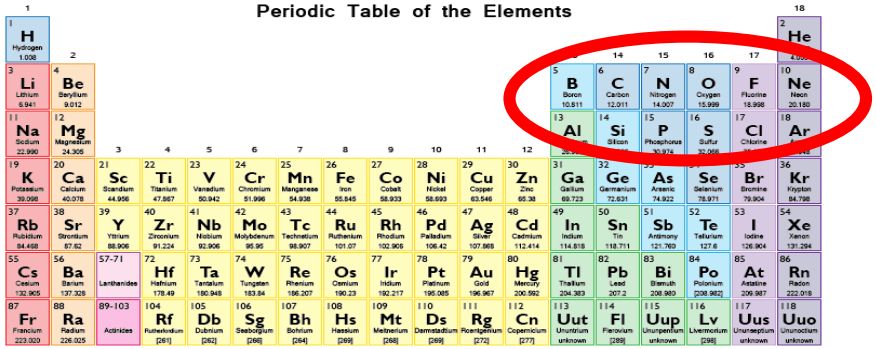


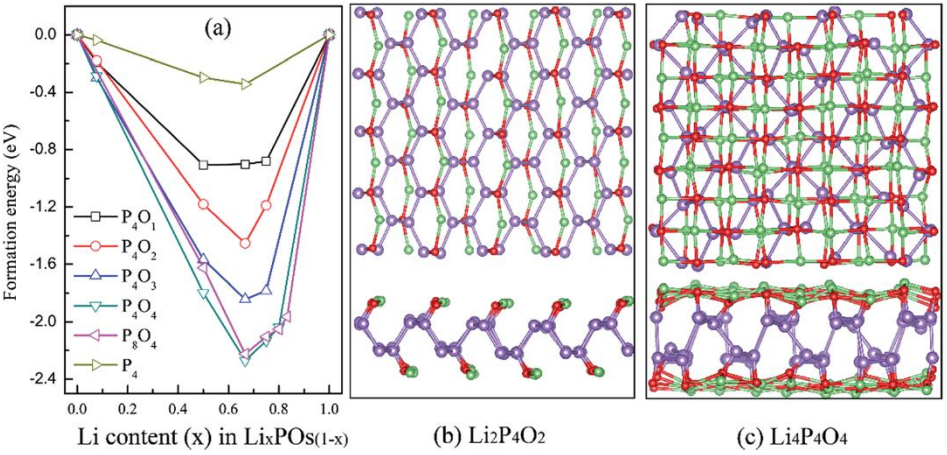
The energy capacity with different Li-S clusters (Wh/kg). 2545 is the pure Li-S theoretical limit.

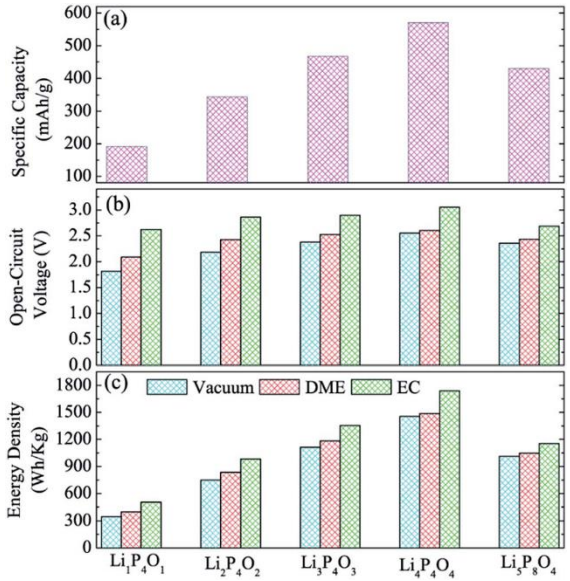
Gao, Pan, Wang, Adv. Energy Mat. 8, 1801823 (2018)

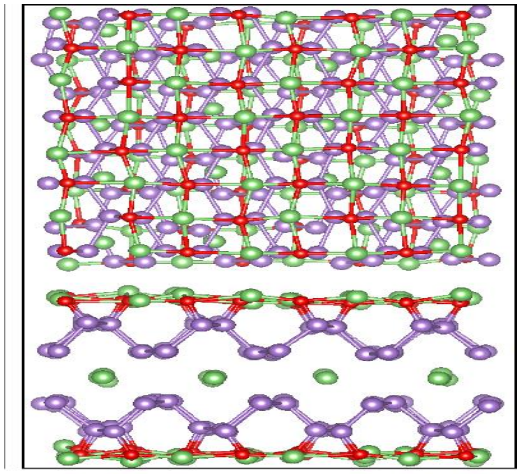
Accomplishments

Using light elements 2D material for Li cathodes: Oxidized black phosphorene









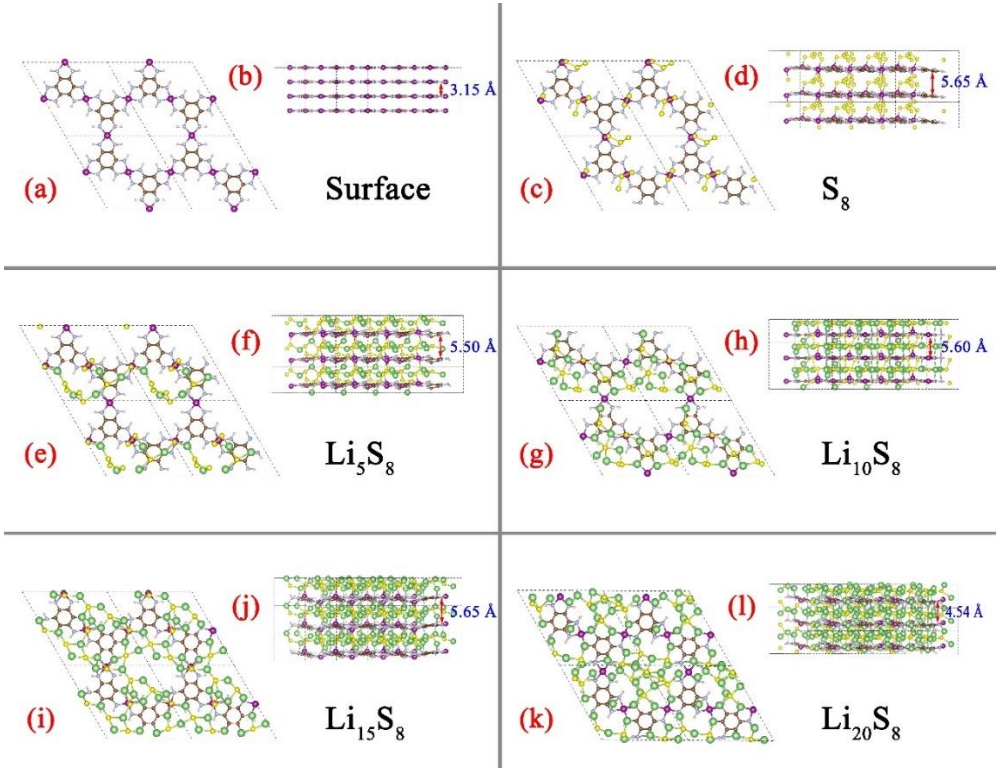
Y. Li, F. Ma, L.W. Wang, J. Mat. Chem. A 6, 7815 (2018)

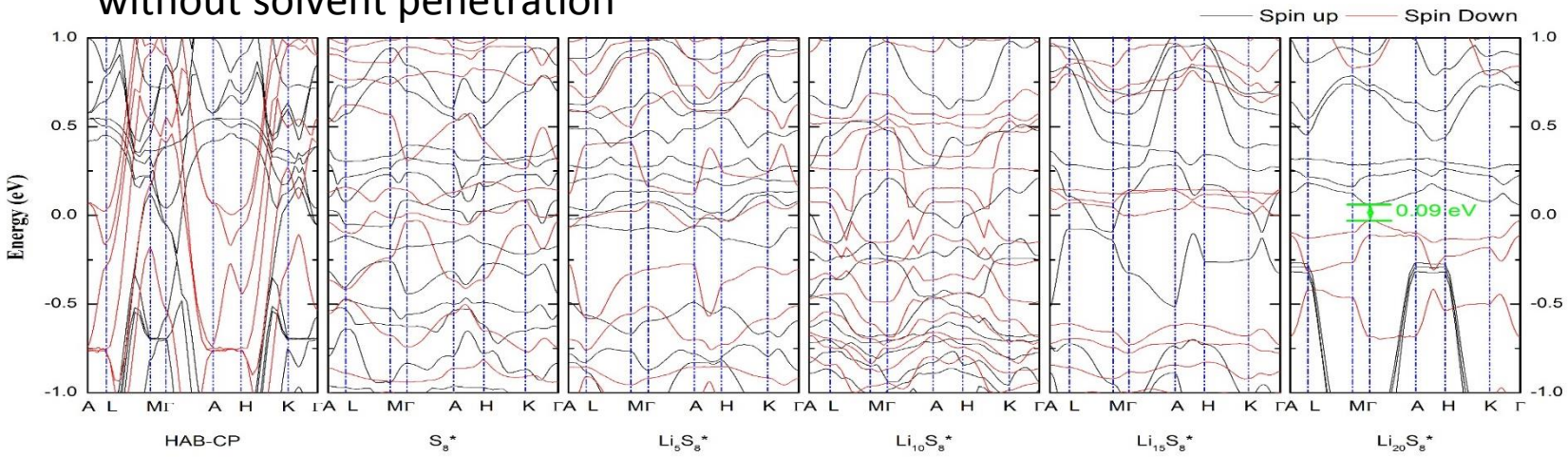
Ab initio MD test for stability

Accomplishments

Design 3D sandwich structure of Li-S cathode: increase volumetric capacity

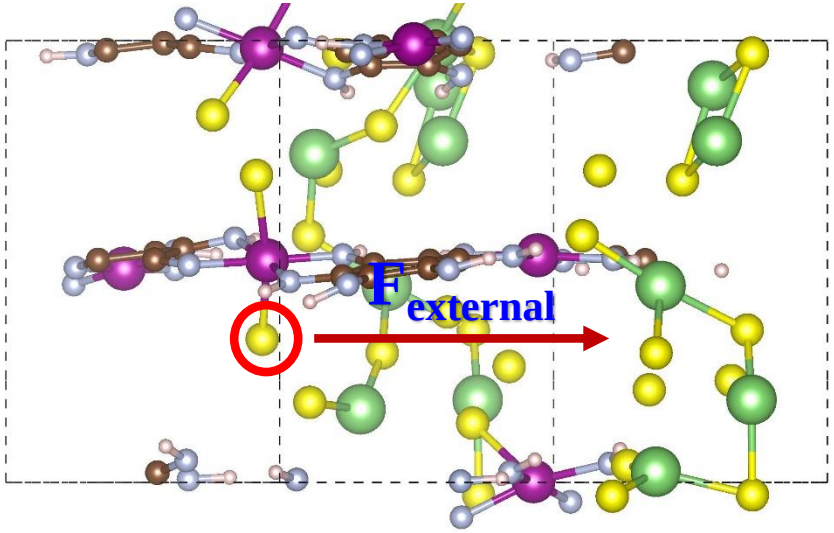
- No significant z-direction expansion during lithiation process
- But lithium diffusion could be an issue
- Design question: can we design a 3D Li-S cathode without solvent penetration

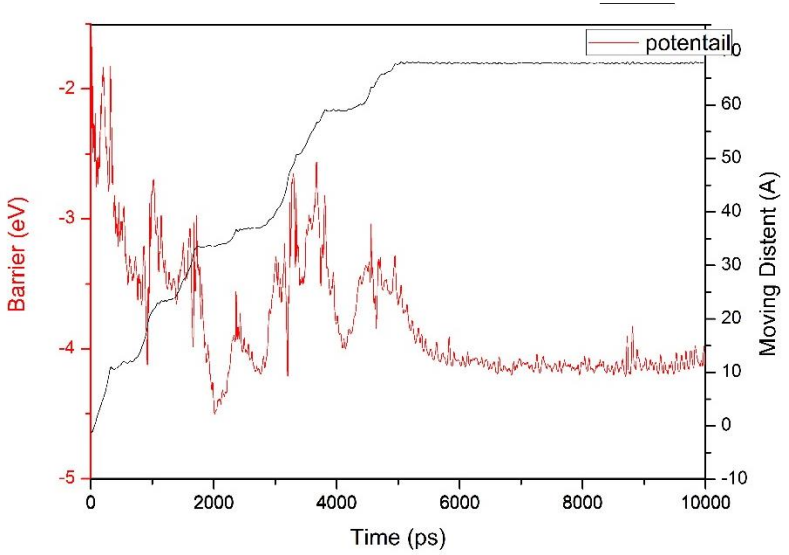


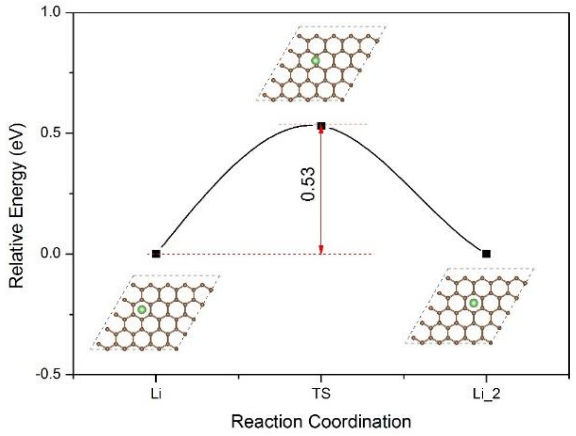


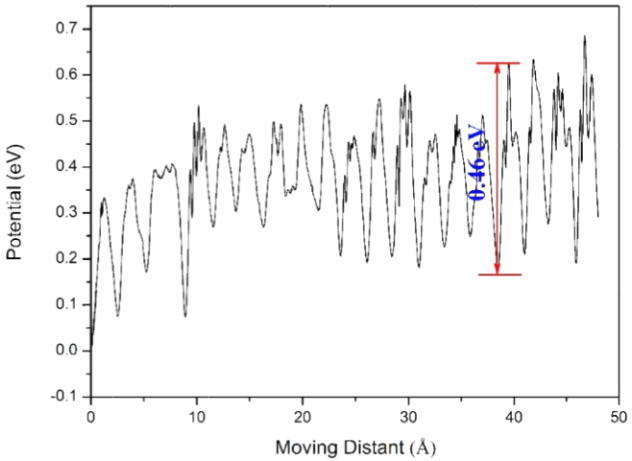
Accomplishments

Develop a new computational approach to study the diffusion barrier in an amorphous material: pull one Li through an amorphous system





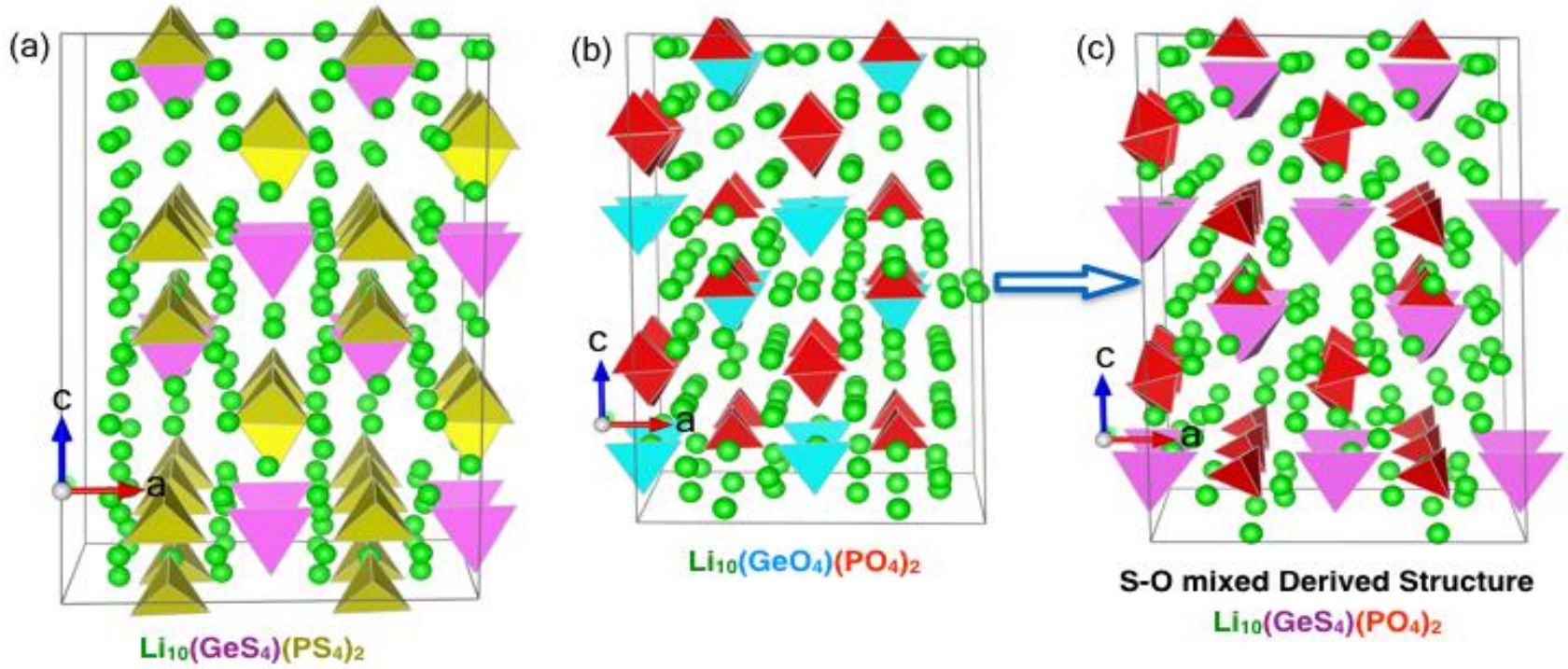




This new method yield similar results as the standard NEB method, but it can be applied to more complex systems

Accomplishments

Improve the solid electrolyte moisture stability:
$Li_{10}GeP_2S_{12}$ to $Li_{10}GeP_2S_4O_8$

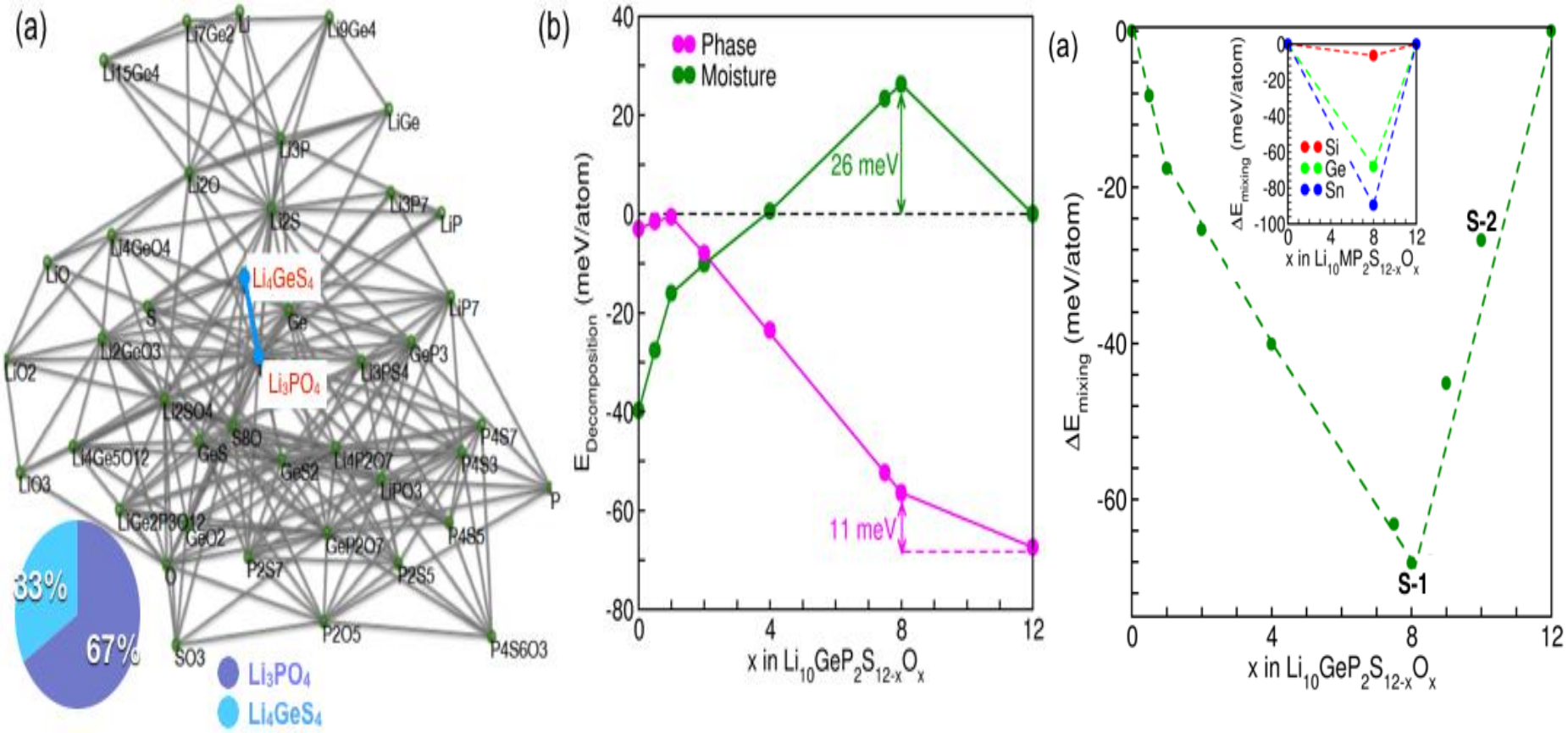


Moisture instability happens at PS_4 tetrahedron $PS_4 + 4H_2O \rightarrow PO_4 + 4H_2S$

Replacing PS_4 motifs with PO_4 motifs

Accomplishments

Stability tests: using linear programing and big data to search for possible decomposition reactions

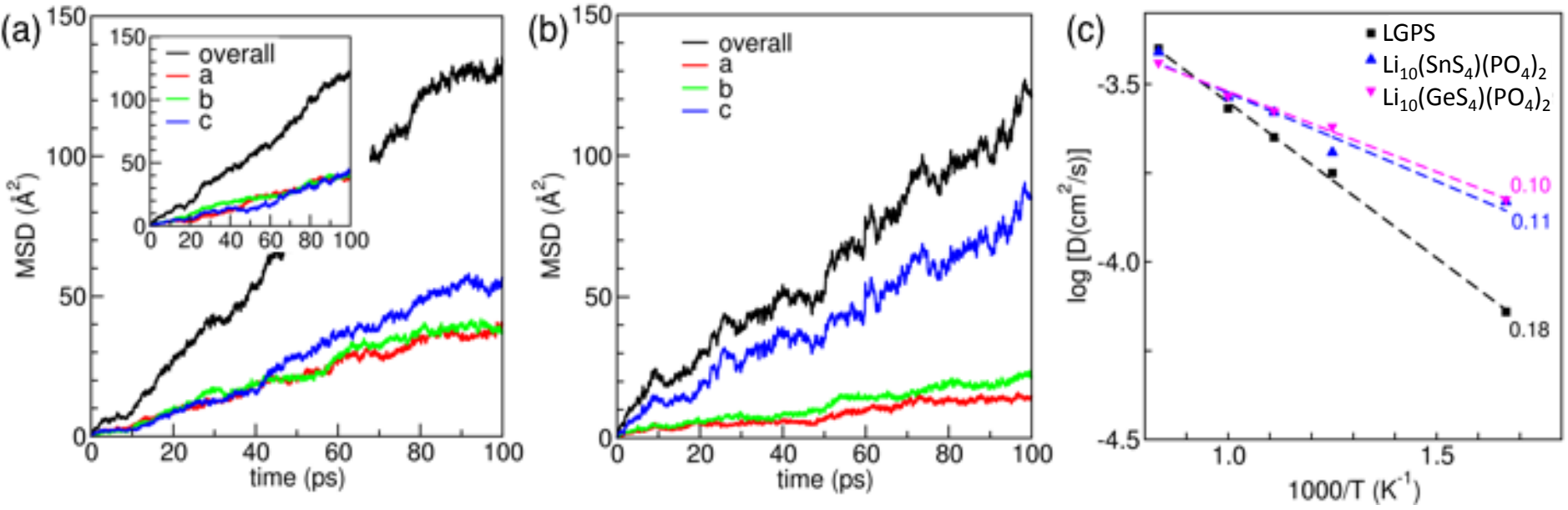


The new compound is stable against the moisture instability

Sn to replace Ge is even better.

Accomplishments

The new compound $Li_{10}GeP_2S_4O_8$ has even a higher Li conductivity than $Li_{10}GeP_2S_{12}$

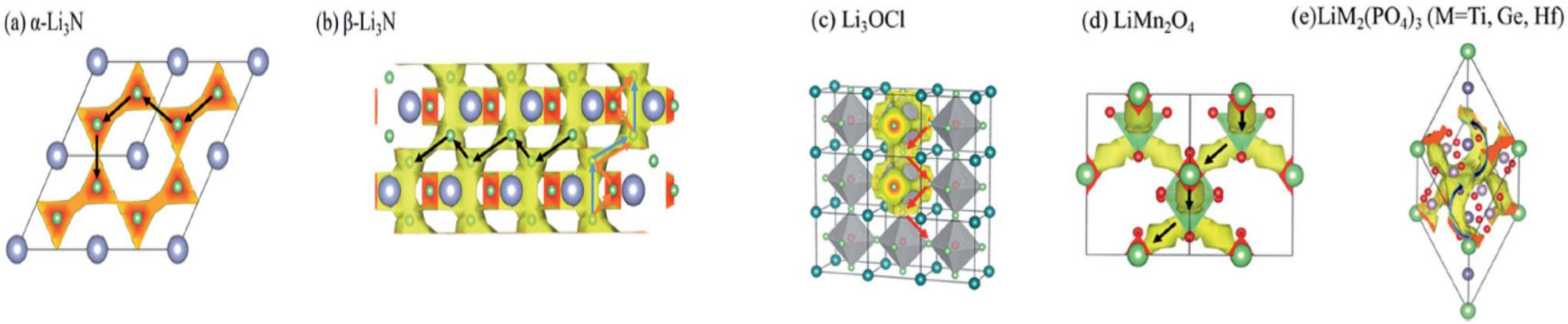


Mean square displacements (MSD) of Li-ions along three different crystallographic directions as well as the overall value, obtained from the ab initio molecular dynamics trajectory at 800 K. (a) for LGPSO: Li10(GeS4)(PO4)2; (b) for LGPS: Li10(GeS4)(PS4)2 (b). The a, b, denotes diffusion in the a, b, c directions. Inset shows the same for LSnPSO: Li10(SnS4)(PO4)2. (c) Li-diffusivity at various temperature.

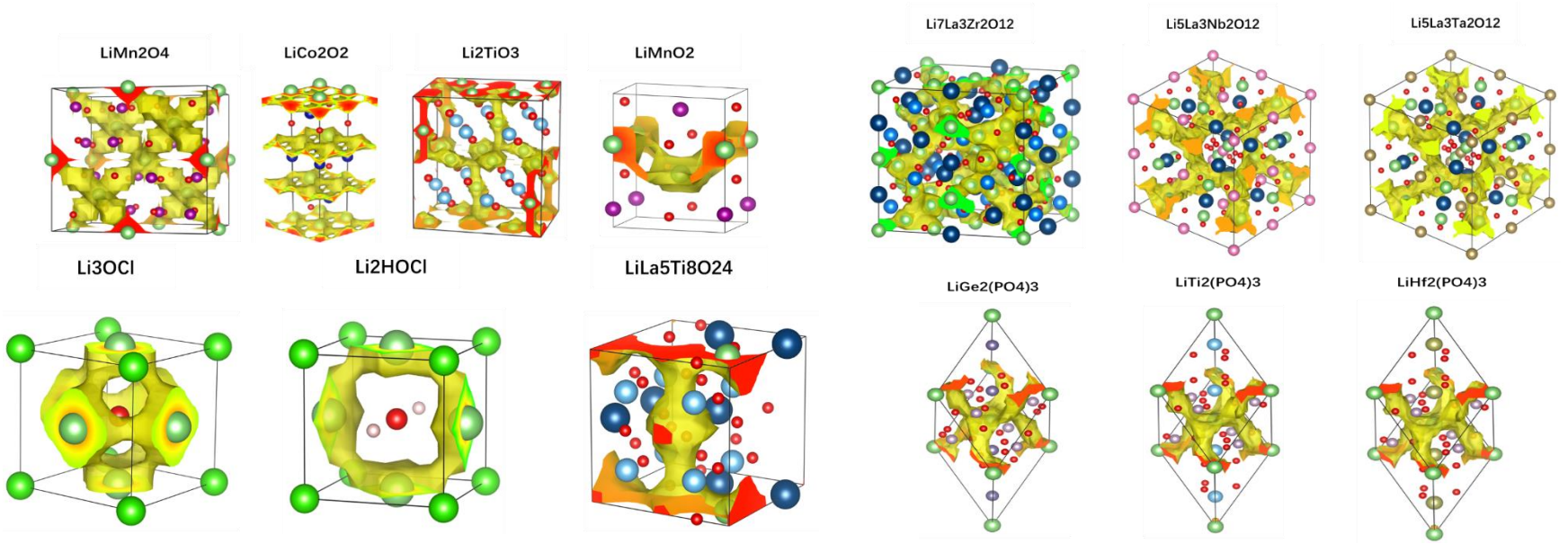
- More distorted system
- More possible path (3D instead of 1D)
- Li goes through LiSxO4-x tetrahedrons, the transition point has lower barrier

Accomplishments

Develop a model screening method for Li diffusion path in solid electrolytes: allow high throughput screening.



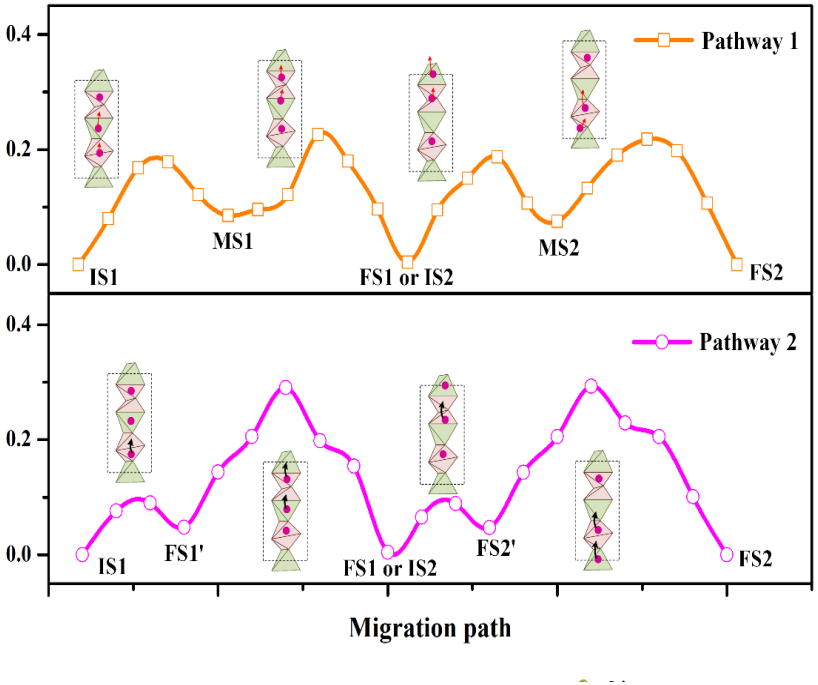
The model results agrees with ab initio calculated results.



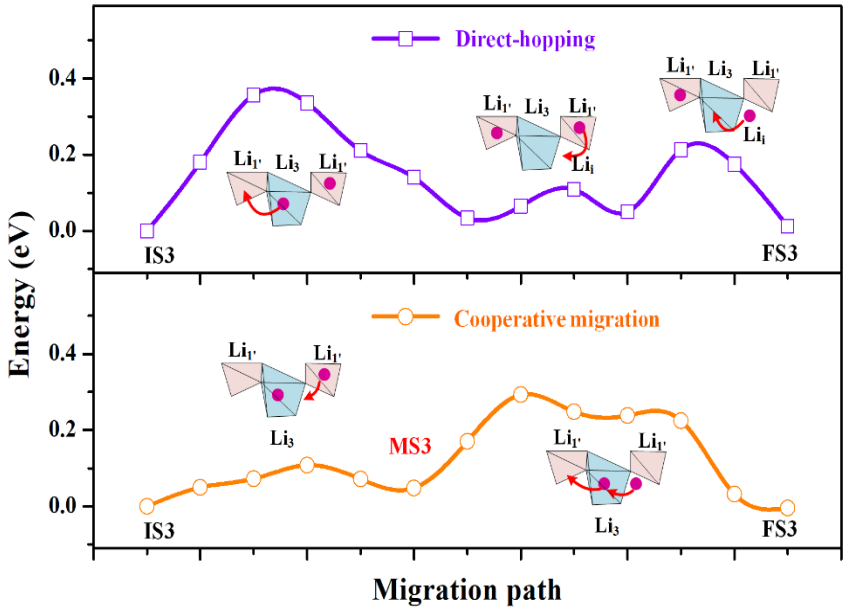
Chen, Jie, Weng, Chen, Pan, Wang, J. Mat. Chem. A 7, 1300 (2019)

Accomplishments

A detailed study of the Li cooperative migration in comparison with the single Li migration in $Li_{10}SiP_2S_{12}$



The energy profiles and sketches of Li-ion cooperative migration along c-axis via pathways 1 and 2, respectively. The cooperative movement is indicated by the two Li movements in some steps



A comparison of a single Li movement path (upper) and cooperative movement path (bottom), and their corresponding energy barriers

Collaborations

- Prof. Yi Cui, Stanford University
  on S attachment on metal and graphene surfaces

- Prof. Zhenan Boa, Stanford University
  on designing redox mediator to facilitate Li2S oxidation

- Dr. Gao Liu, LBNL
  on polymer with S attachment

- Prof. Feng Pan, Peking University
  on various types of battery materials

Remaining Challenges and Barriers

- Accurate determination of Gibbs free energies in solvent
- The molecular structure and aggregation of Li_2S_n in solvent
- Li diffusion in complex amorphous structure
- Large size simulations with long time scale
- Solid electrolyte/metal interface structure and Li diffusion
- Li-S cathode with both high gravitational capacity and volumetric capacity, with high Li mobility

Proposed future work

- Use thermodynamic integration, combine AIMD and classical MD to calculate the Li_2S_n Gibbs free energy
- To study S attachment to 3D frameworks, e.g., black carbon, their morphologies, thermodynamics and solvent/Li^+ diffusion in such materials
- Use genetic algorithm and grand canonical calculations to study surface and interface structures of Li metal and solid electrolyte: stability, morphology, composition and structure
- Study Li diffusion in complex structure using our new pulling atom technique.
- Use linear scale large size ab initio calculation to study solid electrolyte surface and interface.

Summary

- **Objective and Relevance**: using ab initio simulations to understand the underlying mechanism in Li-S reaction process; to design new Li-S cathode materials; to improve the solid electrolyte stability.

- **Approach**: ab initio density functional theory based simulations; genetic algorithm for structure search; large scale simulations.

- **Technical Accomplishments**: Studied several 2D Li-S cathode materials, their capacities and abilities to prevent the dissolution. Proposed a way to improve the LGPS solid electrolyte to improve its moisture stability. Developed a model Hamiltonian to screen the Li diffusion path in solid; developed a Li pulling method to calculate the diffusion barrier in amorphous structure.

- **Collaboration and Coordination**: Yi Cui, Stanford; Zhenan Bao, Stanford, Liu Gao, LBNL; Feng Pan, Peking Univ.

- **Remaining Challenges and Barriers**: Understand the Li2Sn structure in solvent; automatic search for interface structure; accurate calculation of Gibbs free energy

- Proposed Future Work: 3D Li-S cathode design; solid-electrolyte/metal interface; liquid electrolyte calculations

Publications

- D. Chen, J. Jie, M. Weng, S. Li, D. Chen, F. Pan, L.W. Wang, "High throughput identification of Li ion diffusion pathways in typical solid state electrolytes and electrode materials by BV-Ewald method", J. Mat. Chem. A, 7, 1300 (2019).
- Y. Tsao, M. Lee, E.C. Miller, G. Gao, J. Park, S. Chen, T. Katsumata, H. Tran, L.W. Wang, M.F. Toney, Y. Cui, Z. Bao, "Designing a quinone-based redox mediator to facilitate Li2S oxidation in Li-S batteries", Joule 3, 872 (2019).
- Y. Li, F. Ma, L.W. Wang, "Phosphorene oxides as promising cathode material for sealed non-aqueous Li-oxyen battery", J. Mat. Chem. A 6, 2984 (2018).
- J. Wu, L.W. Wang, "2D framworks C2N as a potential cathode for lithium sulfur batteries: an an initio density functional study", J. Mat. Chem. A 6, 2984 (2018).
- G. Gao, F. Pan, L.W. Wang, "Theoretical investigation of 2D hexaaminobenzene coordination polymers as Li-S battery", Adv. Energy Mat. 8, 1801823 (2018).
- L. Yang, J. Zheng, M. Xu, Z. Zhuo, W. Yang, L.W. Wang, L. Dai, J. Lu, K. Amine, F. Pan, "*Short hydrogen bonds on reconstructed nanocrystal surface enhance exygen evolution activity*", ACS Catal. 8, 466 (2018).
- Y. Duan, B. Zhang, J. Zheng, J. Hu, J. Wen, D.J. Miller, P. Yan, T. Liu, H. Guo, W. Li, X. Song, Z. Zhuo, C. Liu, H. Tang, R. Tan, Z. Chen, Y. Ren, Y. Lin, W. Yang, C.M. Wang, L.W. Wang, J. Lu, K. Amine, F. Pan, "*Excess Li-ion storage on nanocrystal reconstructed surface' to boost battery performance*", Nano Lett, 17, 6018 (2017).